Environmentally Friendly Composition

The present invention concerns an environment-friendly composition containing (A) at least one crystalline polycaprolactone (PCL) or a mixture of such polycaprolactones and (B) at least one wax having a melting point in the range between 50°C and 180°C or a mixture of such waxes and (C) optionally further additional substances. The invention also concerns objects produced therefrom and a method for their production.

The inventive composition is excellently suited e.g. for processing in the packaging industry. Thermoplastic compositions are of great importance in the packaging industry, since they are easier to dispose of than conventional plastic materials but have equally good processing and application properties.

It has surprisingly turned out that a composition of the above-mentioned type, having the above-mentioned positive properties, is characterized in that the wax of component (B) is selected from the group of Castor wax, i.e. partially or fully hardened (hydrated) castor oil and/or triglycerides of partially or fully hydrated mono-, di- and/or trihydroxy carboxylic acids and carboxylic acids and/or triglycerides of partially or fully hydroxylated di, tri- and/or polyhydroxy carboxylic acids and carboxylic acids and/or hydroxy carboxylic acid amides and/or hydroxy carboxylic acid salts, wherein the weight ratio between component (A) and component (B) is in the range between approximately 05:95 to 95:05.

Surprisingly, the processibility of polycaprolactones into blown film is considerably improved through the inventive addition of naturally brittle wax and becomes comparable to conventional plastic materials such as

e.g. polyethylene. The produced mixture can be processed with standard blown film systems and without limitations. This is already possible with a composition which contains only the two components (A) and (B) in the absence of further auxiliary processing substances and without substantially changing the mechanical properties of polycaprolactone. The inventive composition surprisingly has a distinct and fast crystallisation behavior even at temperatures of 55-60°C compared to pure polycaprolactone (see DSC curves figures 1-3). Despite the high proportion of relatively brittle wax, such as e.g. brittle castor wax, the flexibility, impact strength and elongation at tear are substantially maintained.

Films which were produced with the inventive composition surprisingly show unexpected soft touch properties after cold-stretching. The invention is defined in the claims with advantageous further developments being given in the dependent claims.

The component (A) of the inventive composition is a crystalline polycaprolactone, preferably a highly crystalline polycaprolactone. It preferably has a molecular weight of approximately 20,000 to 180,000 and a melting range of approximately 50°C to 120°C, preferably 58°C to 62°C and a crystallization temperature of less than 40°C. These polycaprolactones are commercially available, e.g. under the trade name Tone® Polymer P767E and Tone® P787 Polymer (Union Carbide Corp.) or Capa ® 640, Capa ® 650 and Capa ® 680 (Solvay Interox Ltd.).

The component (B) is preferably hardened, i.e. partially or fully hydrated castor oil (castor wax). Castor wax is in general a mixture consisting of glyceryltri-12-hydroxy stearate (approximately 70-99%) and of glycerides (approximately 1-30%) of 12-hydroxy stearic acid, stearic acid and dioxystearic acid. A castor wax is preferably used which consists of

glyceryltri-12-hydroxy stearate (approximately 75-90%) and of glycerides (approximately 10-25%) of 12-hydroxy stearic acid, stearic acid and dioxy stearic acid with a iodine number of 0-5, a melting range of 81-92°C, preferably 83-88°C. This castor wax can be obtained e.g. under the trade name Loxiol ® G 15 (Cognis AG) or simply as hydrated castor oil (OleoChemie AG).

While the component (B) represents preferably hardened, i.e. partially or fully hydrated castor oil (castor wax), the component (B) may, in particular, also comprise a triglyceride of hydrated mono-, di- and/or trihydroxy carboxylic acids and carboxylic acids and/or a triglyceride of hydroxylated di-, tri- and/or polyhydrxy carboxylic acids and carboxylic acids or a mixture of such triglycerides (or of several such triglycerides) with castor wax, wherein the triglyceride has a melting range of 50°C to 180°C, in particular of 70°C to 180°C. Also suitable as component (B) are, in particular, a hydroxy carboxylic acid amide or a mixture of such hydroxy carboxylic acid amides or several such hydroxy carboxylic acid amides with castor wax, wherein the hydroxy carboxylic acid amide has a melting range of 50°C to 180°C, in particular of 70°C to 180°C and a hydroxy carboxylic acid salt or a mixture of such hydroxy carboxylic acid salts or of several such hydroxy carboxylic acid salts with castor wax, wherein the hydroxy carboxylic acid salt has a melting range of 50°C to 180°C, in particular of 70°C to 180°C and is preferably a metallic soap from the group of calcium, magnesium and/or zinc soaps.

Examples of such waxes which can be used as component (B) are listed in table 1.

If a mixture of such a wax or several such waxes with castor wax is used, the proportion by weight of this wax or wax mixture of the component (B) is 1 to 99%, preferably 2 to 70%.

Table 1

No.	chem. Term	trade name	mp.°C	manufacturer
1	partially hydrated castor oil	Castor wax MP 80 Castor wax MP 70	70-80 70-80	NL Industries, Inc. NL Industries, Inc.
2	Triglyceride consisting of mono-, di-, trihydroxy carboxylic acid and carboxylic acids, produced through hydration of epoxidized oil(s), fats, waxes with a high content of oleic acid and/or eruic acid, linoleic acid, linolenic acid and other uni- or poly-unsaturated fatty acids produced from rape oils, olive oils, sunflower oils, castor oil, triolein, soy oils, linseed oils and other oils	(a) EDENOL 81/82 (a) EDENOL B35 (a) EDENOL B316	Liquid Liquid Liquid	Cognis / Henkel Cognis / Henkel Cognis / Henkel
3	Trigylycerides consisting of di-, tri-, polyhydroxy carboxylic acids and carboxylic acids, produced through hydroxylation of uni- and poly-unsaturated oils (b), fats and waxes	(b) soy oils (b) rape oils (b) sunflower oils (b) castor oils (b) olive oils		

		(b) linseed oils (b) other native oils		
4	Hydroxy carboxylic acid amides			
5	Hydroxy carboxylic acid salts, in particular of Ca, Mg, Zn	LIGA Calcium-12-oxy stearate magnesium-12-hydroxy stearate	135-155 120-140	Greven Fettchemie Bärlocher

The waxes of component (B) - see table 1, examples 1 to 3 - consist of esters of glycerine which contain linear, branched or cyclic, partially saturated or saturated, partially hydrated or fully hydrated, dimerized and polymerised hydroxy carboxylic acids and/or carboxylic acids. Esters of the glycerine conventionally contain at least a residue of an acid and at least a residue of the polyol glycerine. The esters or waxes used in accordance with the invention are known per se. The hydroxy carboxylic acid esters of the glycerine to be used in accordance with the invention contain residues of (C_1-C_{40}) hydroxy carboxylic acids and (C_1-C_{40}) carboxylic acids with molecular weights in the range between 40 and 2,000.

Further waxes suitable as component (B) – see table 1, example 4 – include amides which contain linear, branched or cyclic, partially saturated or unsaturated, partially hydrated or fully hydrated, dimerized and polymerized hydroxy carboxylic acid amides. Hydroxy carboxylic acid amides conventionally contain at least a residue of a hydroxy carboxylic acid and at least a residue of an amide group. The amides or waxes used

in accordance with the invention are known per se. The hydroxy carboxylic acid amides to be used in accordance with the invention contain residues of (C_1-C_{40}) hydroxy carboxylic acids with gram-molecular weights in the range of 40 to 2,000.

Further waxes suitable for component (B) - see table 1, example 5 - include metallic soaps of a hydroxy carboxylic acid, preferably on the basis of calcium, magnesium- and zinc soaps which are linear, branched or cyclic, partially saturated or unsaturated, partially hydrated or fully hydrated, dimerized compounds. Such metallic soaps contain at least one hydroxy carboxylic acid residue which forms fatty acid salts (metallic soaps) with monovalent metals such as lithium, sodium, potassium and with bivalent or multivalent metals such as magnesium, calcium, aluminium, zinc and iron. The metallic soaps on the basis of hydroxy carboxylic acids to be used in accordance with the invention preferably have a chain length of C_1-C_{40} and a gram-molecular weight in the range of 40 to 2,000 and have mono-, bi- and multivalent metals.

The inventive composition may contain further substances (component C) in addition to the components (A) and (B). These additional substances are e.g. fillers, sliding agents, plasticising agents, modificators (tensile strength, rigidity, impact strength, resistance to tear propagation and processing viscosity) and stabilizers, flame retardants, colorants, inorganic and organic pigments, carbon black, foaming agents or other additives known per se in polymeric chemistry. These additives have functional properties such as antistatics, antifogging, fungicides, pesticides, herbicides, fertilisers etc. The additives are added to the composition in amounts known per se.

Fillers are e.g. titanium dioxide, calcium carbonate, dolomite, iron oxides, talcum, kaolin, mica, bentonite, magnesium oxide, silicium dioxide

pyrogen or precipitated, aluminium oxide, chitosane, cellulose fibers or plant fibers, hemi-cellulose, cellulose ester, cellulose ether, starch ester, starch ether, hydroxy alcyl cellulose, hydroxy alcyl starch, ceramic powder or wood. The fillers are preferably used in a portion by weight of 3-40%, preferably 5-25%, in particular 10-20% relative to the overall weight of the composition depending on the type.

Sliding agents are e.g. calcium stearate, aluminium stearate, magnesium stearate, fatty acid amides/imides, lecithines, mono- or diglycerides contained in a concentration between 0.5 and 5 % by weight, preferably 0.7 to 1.5 % by weight relative to the overall weight of the composition.

Plasticising agents are e.g. polyalkylene oxides, preferably polyethylene glycols or polypropylene glycols whose terminal hydroxylic groups are estered or ethered, ethylene glycol, propylene glycol, sorbitol, glycerine, mono- and/or poly glycerine, glycerine mono-, di- or triacetate, urea, glycine, proline, zein, pentaerythrite, triethylcitrate, tributylcitrate, fatty alcohols, such as stearyl alcohol and further plasticising agents known per se.

Modificators of the tensile strength, rigidity, impact strength, resistance to tear propagation and processing viscosity are e.g. other commercially available biologically degradable materials (BAW) such as polyester, copolyester (Ecoflex BASF), polyhydroxy carboxylic acids (Ecopla Dow/Cargill), polyester amides (BAK Bayer), other BAWs and calcium-, magnesium-, zinc salts of hydroxy carboxylic acids and of urea acids; as well as crystalline polyoles and polyol/ether compounds such as e.g. Di(trimethylol propane). Similar modifications are obtained through substances such as talcum, layer silicates and plant fibers. These modificators are contained in concentrations of 0.1-30 % by weight, preferably 1-20 % by weight, preferably 2-10 % by weight.

Stabilisators are e.g. antioxidants, UV absorbers, UV quenchers, bactericides or fungicides known per se which are used in amounts known per se.

Flame retardants are e.g. compounds containing nitrogen, phosphor, sulfur or halogen or mixtures thereof. Such flame retardants are known per se. The flame retardants are contained, in particular, in amounts of 0.1 to 10 % by weight, preferably 1-6 % by weight and most preferred 2-4 % by weight relative to the overall weight of the composition.

Inorganic or organic pigments, preferably conventional biologically degradable or ecologically compatible colorants/pigments are used as colorants in amounts known per se. Nucleation means are e.g. the mentioned fillers or magnesium silicate (microtalcum) of a particle size of between 0.1 and 5μm. These are preferably contained in a concentration of 0.1-3 % by weight, preferably 0.1-0.5 % by weight.

Foaming agents are known per se, e.g. a combination of sodium bicarbonate and citric acid and similar commercially available foaming agents. It is also possible to directly add gaseous nitrogen or carbon dioxide to the molten composition in the extruder. It is also possible to mix the inventive composition with calcium carbonate and 12-hydroxy stearic acid during an extrusion process and foam it with the generated carbon dioxide. The foaming agent is preferably added in a concentration between 0.1-2 % by weight relative to the overall weight of the composition.

The inventive composition can be processed like conventional thermoplastic materials using a conventional device which is suited e.g. for tubular film production, blow molding, extrusion and coextrusion (rod,

tube and film extrusion), press forming, injection molding processing, doctoring, foaming, casting methods or further processing methods known per se to produce objects known per se. These articles include e.g. foils, bags, sacks, tubes, rods, bottles, cups, packaging materials and other conventional objects in all processing stages from powders, granulated matter and intermediate products to finished products. To vary the properties, the above-mentioned objects can be produced in one layer, several layers or another manner known per se. The inventive composition can thereby be combined with other materials and be used as surface and/or carrier layer. The foils may thereby be further processed in the unstretched and cold- or warm-stretched state. The cold-stretched foils are very soft and have a so-called soft touch. These objects are mainly used in areas where disposal has been a major problem up to now such as e.g. in the field of agriculture as agricultural foil or plant pots, in the field of disposal as composting bags, in the field of packaging as carrier bags, shrinking foils, shampoo bottles, cups or cutlery. Moreover, e.g. tube foils for the production of bags and sacks, agricultural foils, injection- and blow-molded articles, hot melts and fillers can also be produced. Water-sensitive products can also be surface coated. The soft stretched foils can constitute a barrier layer to prevent the "wetting through" of paper fleeces e.g. for paper tissues or other hygienic applications.

The inventive composition can be produced in different ways e.g. through stirring the molten components (A) and (B) in a container and simultaneous or subsequent addition of additives; mixing of all components in single-screw extruders, double-screw extruders with identical or opposite motion, planetary roller extruders, pumping of the components into a static mixer or through other suitable mixing methods known per se which are suited for homogeneously mixing the components due to their temperature control, shearing, pressure and retention times.

It is also possible to produce intermediate materials which can then be processed into the inventive product.

The inventive mixtures are characterized by an adjustable melt viscosity permitting easy processing of various applications from paper coating to blown foil. The elasticity or rigidity can be largely varied to thereby obtain either comparatively rigid or elastic foils.

Examples 1 through 6, comparative examples 7 and 8

Methodology:

Laboratory Z vacuum kneader with delivery screw (LINDENLK III 1 A) mixing and delivery region in V4A steel (material no.: 1.4571 / 1.4581)

Oil thermostat:	(Lauda USH 400)
Dosing vibration channel:	(Fritsch Laborette)
Granulator:	(Collin CSG 171 T)

Methodology for examples 1 through 6:

Polycaprolactone [component (A)] is added to the laboratory kneader in batches via a dosing channel and melted at 120°C mass temperature. Castor wax [component (B)] is added under further mixing and kneading. Due to the high portion of castor wax, an inhomogeneous mixture is initially formed during 15-20 minutes at 120°C until a homogeneous and kneadable mixture is also obtained through diffusion and distribution. After another 15 minutes of kneading, the mixture is quickly cooled to 90-95°C and subsequently extruded into a strand via the delivery screw through the hole nozzle. This strand is cooled in a water bath and

subsequently granulated. During processing, good mixing and kneading must be ensured. The individual compositions are shown in table 2.

Example no.		1	2	3	4	5	6	7	8
Tone® P787	Union Carbide	300g	350g					500g	
Capa ® 680	Solvay			300g	350g				500g
Capa ® 650	Solvay					300g	350g		
Loxiol® G15	Cognis	200g	150g	200g	150g	200g	150g		
DSC curve		Fig. 2	Fig. 3					Fig. 1	

In table 2:

Tone ® P787: PCL, molecular weight approximately 80,000
melting point approx. 60-62°C
MFI 1.0 (125°C) ASTM D1238-73)

Capa® 680: PCL, molecular weight approx. 80,000
melting point approx. 60-62°C
crystallization temperature 27.4°C
crystallinity 56%
MFI 0.6 (80°C, 2.16 kg g/10 min)

Capa® 650: PCL, molecular weight approx. 50,000
melting point approx. 60-62°C
crystallization temperature 25.2°C

crystallinity 56%
MFI 2.36 (80°C, 2.16 kg g/10 min)

Loxiol® G15: castor wax, melting point 83-90°C
iodine number 0-5
acid number 0-5
saponification number 175-185
hydroxylic number 140-165

The compositions of examples 1 through 6 are characterized by excellent processing properties which can be demonstrated in particular for the production of foils. For the production of blown foil it is advantageous when the processed materials have a distinct crystallization point (see DSC curves, figures 2 and 3) which is clearly above room temperature such that the foil can be easily solidified after leaving the nozzle through air cooling. This is not the case for pure PCL (comparative examples 7 and 8, see DSC curve figure 1), since the crystallization region is < 35° and therefore special cooling must be used for solidification. This is not required for the compositions of examples 1 through 6, since the crystallization temperature is approximately 58°C. Pure castor wax is brittle and cannot be processed into blown foil through extrusion.

Mixtures with highly molecular PCL showed a very good blow behavior for the production of blown foils. It was thereby possible to reduce the processing viscosity and therefore also the torque and processing temperature with increasing wax content; the crystallization temperature of the composition did not change substantially when the wax content varied. Even for large wax content (40 % by weight) of the inventive composition, the mechanical properties obtained were almost equal to those of pure polycaprolactone. It was also possible to obtain very thin

foils of down to 8µm which is unusual for biologically degradable materials.

Addition of a further wax has shown that the combination of several waxes for component B of the inventive composition permitted more variable setting of the melt viscosity. Higher viscosities can thereby be achieved as are required e.g. for deep drawing and blow forming. This component also increases the viscosity and rigidity of the products.

Due to the distinct gelling behavior of the metallic soaps, premixing of the components of table 3 (examples 9-11) proves to be advantageous and permits pinhole-free mixing of the inventive composition. These mixtures permit an increase in the processing viscosity compared to example 15 and an improved crystallization behavior compared to the initial compound polycaprolactone (CAPA 680).

Examples 9 through 12:

Method for producing a pre-mixture:

Magnetic stirrer with heating plate IKAMAG RCT (Jahn and Kunkel) 1.5 l stainless steel pot (conventional)

Laboratory stirring machine: (Heidolph RZR 50 L)

Laboratory stirring tool: (propeller head: 100mm)

Method for producing a pre-mixture (examples 9 through 11)

LOXIOL® G15 [component (B)] is added in batches to the stainless steel pot and melted at 120°C mass temperature while stirring (50-200 R/min). LIGA® calcium-12-oxystearate (see examples 9-11) is added as component (B I) while continuing to mix (200-500 R/min) and the mixture

is heated to 160°C. The mixture is then cooled to 140°C and poured into a Teflon-coated tub and solidified into a plate. This plate is ground with a grating machine (Schulte) - grating insert 1 for fine grain - and further processed (see table 4 and examples 12-14).

Table 3:

Examples no.		9	10	11
Loxiol ® G15 (B)	Cognis	475 g	450 g	400 g
LIGA® 12-oxy stearate (B I)	Greven Fettchemie	25 g	50 g	100 g

In table 3:

Loxiol® G15: (castor wax)
melting point 83-90°C
iodine number 0-5
acid number 0-5
saponification number 175-185
hydroxylic number 140-165

LIGA® calcium-12-oxy stearate: (calcium-12-hydroxy stearate)
melting point 135-147°C
free fatty acid < 1%
moisture < 3%

Examples 12 through 14, comparative example 15

Method structure:
Laboratory Z vacuum kneader with delivery screw (LINDEN LK III 1A) mixing and delivery region in V4A steel (material no.: 1.4571 / 1.4581)

Oil thermostat: (Lauda USH 400)
Dosing vibration channel: (Fritsch Laborette)
Granulator: (Collin CSG 171 T)

Procedure for examples 12 through 14, comparative example 15:

Polycaprolactone [component (A)] is added in batches to the laboratory kneader via a dosing channel and melted at 120°C mass temperature. The ground pre-mixtures of examples 9-11 are added as [component (B)] thereby further mixing and kneading. After a further 15 minutes of kneading at 120-160°C, the mixture is quickly cooled to 100-110°C and subsequently extruded into a strand by the delivery screw via the hole type nozzle. This strand is cooled in the water bath and subsequently granulated. Good mixing and kneading must be ensured during processing. The individual compositions are combined in table 4.

Table 4:

Examples no.		12	13	14	15
Capa® 680	Solvay	300g	300g	300g	300g
Pre-mixture	Example no. 9	200g			
Pre-mixture	Example no. 10		200g		
Pre-mixture	Example no. 11			200g	
Loxiol G 15	Cognis				200g

In table 4:

Capa® 680: PCL molecular weight approx. 80,000
melting point approx. 60-62°C,
crystallization temperature 25.2°C
crystallinity 56%
MFI 0.6 (80°C, 2.16 kg g/10 min)

Pre-mixture examples 9 through 11: see table 3